

On the other hand, platinum 5d orbitals project further into space than palladium 4d orbitals. Therefore, one would predict that substitution of KOPD with the analogous platinum salt should increase the degree of metal-adjacent ligand overlap and, consequently, result in an increase in the mobility of the charge carrier in the host.

From the initial photolysis results it appears that reduction of Cu^{2+} does not occur at those metal ions positioned adjacent to the photodecomposed oxalate ligands. We base this conclusion on the fact that we could detect no apparent reduction in the total epr signal intensity from the Cu^{2+} ions during exposure. However, we did note that the Cu^{2+} spectra were modified as the photolysis proceeded. The end product of this exposure was probably CuC_2O_4 isolated in the KOPD environment. This photodecomposition of a

single, coordinated oxalate ligand at each impurity-ion site would account for the detection of four magnetically inequivalent sites per unit cell occupied by the cupric ion product. The photoproduced electron must be transmitted through the KOPD crystal to be trapped at a distant $[\text{Pd}(\text{C}_2\text{O}_4)_2]^{2-}$ complex or a lattice defect.

To simplify the task of analysis we are now attempting to follow the photolysis of single crystals of KOPD containing minute quantities of ^{63}Cu (99%). Isotopic enrichment will halve the number of hyperfine lines originating from the copper-containing decomposition products, which should facilitate a complete spectral analysis.

Registry No. $\text{K}_2\text{Pd}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, 36425-78-2; copper, 7440-50-8.

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario, Canada

Chemistry of Metal Hydrides. XV. Mechanism of Double-Bond Migration Induced by Platinum(II) Hydrides

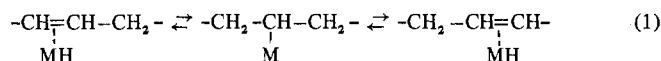
H. C. CLARK* and H. KUROSAWA

Received November 30, 1972

The mechanism of double-bond migration induced by some platinum(II)-hydrido complexes has been investigated using platinum(II)-deuterido analogs as well as 2-deuterated allyl methyl ether. Both the stoichiometric reaction of diallyl ether with Pt-H and the catalytic conversion of allyl alkyl ethers with Pt-H to *cis*-propenyl alkyl ethers were found to involve the initial reversible anti-Markownikov addition of Pt-H across the terminal C=C bond before double-bond migration occurs. Double-bond migration may be achieved through attack by hydridic hydrogen on the terminal carbon and elimination by platinum of another hydrogen atom from allylic carbon. The reaction of butene-1 with Pt-H proceeded similarly.

Introduction

Some transition metal complexes are known to catalyze the migration of C=C bonds in olefinic compounds. Several mechanisms have been proposed¹ to account for this homogeneously catalyzed isomerization, although no single mechanism fully explains all aspects of systems with different transition metal complexes. One of the simplest mechanisms suggested involves the reversible addition of the M-H bond across C=C, so that the formation of the metal hydride and of the hydrido(π -olefinic) complex may well be key steps in the overall reaction



We have previously discussed² the facile insertion of olefins into the Pt-H bond, in which the formation of the four-coordinate intermediate *trans*-[PtH(PR₃)₂(olefin)]⁺ from coordinatively unsaturated platinum(II)-hydrido complexes plays an essential role. In extending these studies, we found³ that double-bond migration and insertion take place readily in the stoichiometric reactions of allylic derivatives with such reactive platinum(II) hydrides as *trans*-[PtH(PR₃)₂(acetone)]⁺ and *trans*-PtH(ClO₄)(PPh₃)₂. More generally, these reactive platinum(II) hydrides were found to be capable

of catalyzing the isomerization of butene-1, allyl methyl ether, and allyl phenyl ether at ambient conditions. The present paper describes a series of experiments on both the stoichiometric and the catalytic isomerization of some allylic compounds with platinum-hydrido complexes involving 2-deuterated allyl methyl ether as well as platinum(II)-deuterido complexes. Our results are consistent, in part, with the mechanism proposed by Cramer and Lindsey,⁴ who suggested that the isomerization of olefins with platinum(II) complexes involves both Markownikov and anti-Markownikov addition of Pt-H across the terminal C=C bond.

Results and Discussion

Reaction of *trans*-PtDX(PR₃)₂ with (CH₂=CHCH₂)₂O. In a previous paper,³ we suggested that the sequence 2 was involved in the reaction of some platinum(II)-hydrido complexes with allylic ethers. *trans*-PtD(ClO₄)(PPh₃)₂ (II) and *trans*-PtD(NO₃)(PPh₂Me)₂ (IIId) have now been used with (CH₂=CHCH₂)₂O in order to investigate the mechanism of the isomerization process. In both reactions, the deuterium distribution in the reaction product, CH₃CH₂CHO, was determined from the proton nmr and mass spectra of the 2,4-dinitrophenylhydrazone adduct⁵ of propionaldehyde (Table I).

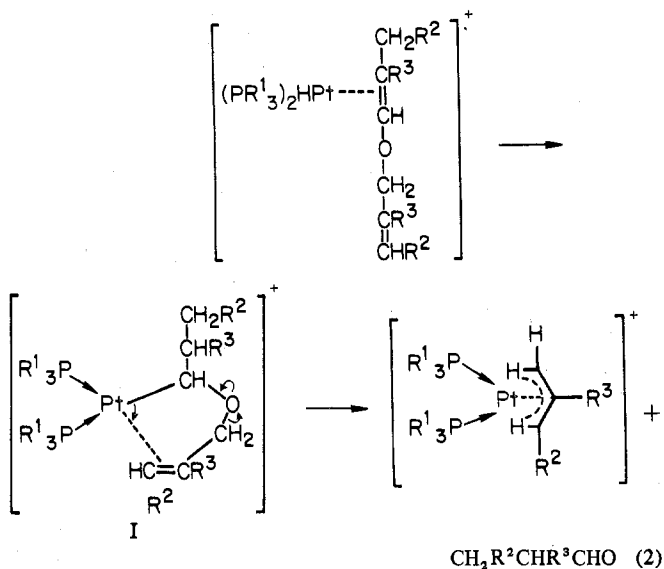
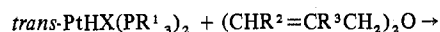
Anti-Markownikov addition of Pt-D across the terminal C=C bond (*k*₂) (see Scheme I) and reversible elimination of

(1) See, for example, R. S. Coffey, "Aspects of Homogeneous Catalysis," Vol. 1, R. Ugo, Ed., Manfredi, Milan, 1970, p 1; F. R. Hartley, *Chem. Rev.*, 69, 799 (1969), especially p 838.

(2) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 11, 1275 (1972).

(3) H. C. Clark and H. Kurosawa, *Chem. Commun.*, 150 (1972); *Inorg. Chem.*, 12, 357 (1973).

(4) R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, 88, 3534 (1966).



Pt-H from an anti-Markownikov adduct (k_{-2}') are responsible for deuterium incorporation at methylene group. An alternative explanation which does not invoke such anti-Markownikov addition would involve an insertion process arising from intermediate π -olefinic complexes formed by Pt-D and the newly produced $\text{CH}_3\text{CH}=\text{CHOR}$ or $\text{CH}_2\text{DCH}=\text{CHOR}$ moieties to give $\text{CH}_3\text{CHDCH}(\text{OR})\text{Pt}$ or $\text{CH}_2\text{DCHDCH}(\text{OR})\text{Pt}$. However, an almost negligible amount of $\text{C}_3\text{H}_4\text{-D}_2\text{O}$ species observed in the reactions using IID as shown in Table I apparently rules out the formation of such a π complex of Pt-D with propenyl derivatives. Thus, it seems that displacement of coordinated propenyl groups is very slow in the reactions using IID. Furthermore, the absence of $\text{C}_3\text{H}_4\text{D}_2\text{O}$ species also excludes the intermolecular exchange of coordinated allyl groups involved in IV and IV' in the scheme when IID is used. The insignificance of such olefin exchange is also supported by the fact that the total deuterium content of IID was retained in $\text{CH}_3\text{CH}_2\text{CHO-d}$ regardless of the ratio $[(\text{C}_3\text{H}_5)_2\text{O}]/[\text{PtD}]$, even though the displacement of $\text{CH}_2=\text{CDCH}_2\text{OR}$ in IV' by nondeuterio allyl groups should cause the loss of the total deuterium content, a process which should be more prominent in the overall reaction at higher $[(\text{C}_3\text{H}_5)_2\text{O}]/[\text{PtD}]$ ratios. A slightly different behavior is apparently involved in reactions using IIId. The appearance of a small amount of $\text{C}_3\text{H}_4\text{D}_2\text{O}$ species and the loss of the total deuterium content on going from IIId to $\text{CH}_2\text{CH}_2\text{CHO-d}$ are indicative of relatively rapid olefin exchange processes involving IV and IV'. In particular, the fact that the decrease in deuterium incorporation on going from $[(\text{C}_3\text{H}_5)_2\text{O}]/[\text{PtD}] = 1:1$ to $6:1$ is more pronounced at the methylene than at the methyl groups of $\text{CH}_3\text{CH}_2\text{CHO-d}$ is in good agreement with such an exchange reaction of allyl groups. Thus the enhanced degree of allyl exchange in the presence of excess amounts of diallyl ether would cause a decrease in deuterium incorporation mainly at the methylene group through the displacement of the coordinated $\text{CH}_2=\text{CDCH}_2\text{OR}$ by nondeuterio allyl groups.

(5) The proton nmr spectra showed that the relative intensities of the peaks corresponding to methyl, methylene, and aldehyde protons in the original $\text{CH}_3\text{CH}_2\text{CHO-d}$ are almost the same as in the 2,4-dinitrophenylhydrazone adduct, indicating that no proton-deuterium exchange occurred during the formation of the 2,4-dinitrophenylhydrazone adduct. This is supported by the fact that in the reaction using IID the total deuterium content of the adduct is only slightly less than that of the original IID.

It is also interesting that neither dipropenyl ethers nor allyl propenyl ethers were produced even in the presence of excess amounts of diallyl ether relative to the amount of IID or IIId. This may be a result of the slow displacement of coordinated propenyl groups in VII or VII' by other C=C bonds as described earlier and/or the much greater rate of the reaction in step k_5 or k'_5 , which can be attributed to the existence of an additional C=C bond within the molecule capable of stabilizing the intermediate of type I. For the same reason the reverse process of k_4 or k'_4 may well be very slow. In the absence of any such chelating group, catalytic formation of propenyl derivatives occurred in the reaction of allyl methyl ether or allyl phenyl ether with some platinum-(II) hydrides (see later). A similar stabilizing effect due to chelation involving the C=O group was suggested in the stoichiometric reaction of allyl acetate with platinum(II)-hydrido complexes.³

The ratio of k_3/k_2 as well as the kinetic isotope effect in the steps involving the addition and elimination of Pt-D may affect the relative deuterium incorporation at methyl and methylene groups. If any kinetic isotope effect can be neglected and if allowance is also made for the fact that the reverse of the step k_3 or k'_3 is very slow,⁴ it is possible to estimate k_3/k_2 as approximately $1/2$ using the observed deuterium incorporation pattern in the reactions with IID where olefin exchange is almost negligible. However, it is also possible that k_3/k_2 is smaller than $1/2$ or may approach zero if the position of equilibrium between IV and IV' lies in favor of IV. A similar difference in the positions of the equilibria involved in the reactions of Pt-H with $\text{CH}_2=\text{CDCH}_2\text{OME}$ and of Pt-D with $\text{CH}_2=\text{CHCH}_2\text{OME}$ is also observed in the isomerization of $\text{CH}_2=\text{CDCH}_2\text{OME}$ with platinum(II) hydrides (see later).

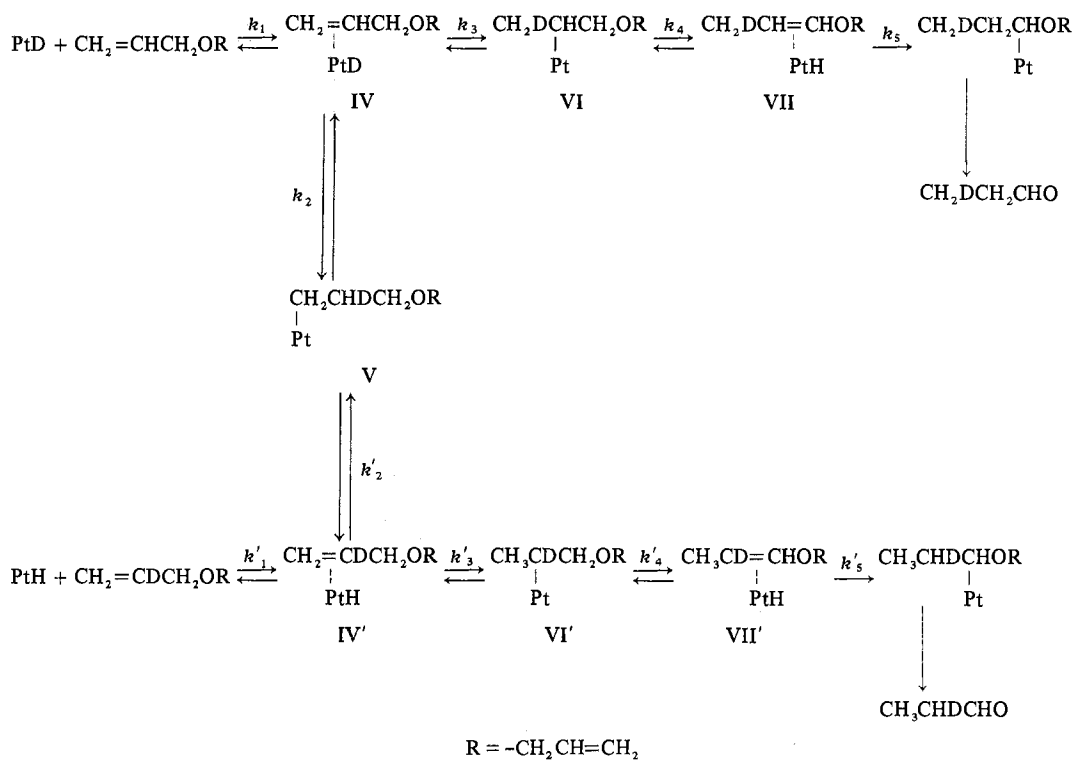
Isomerization of Allyl Methyl Ether and Allyl Phenyl Ether. We previously reported³ the ready isomerization of allyl methyl ether and allyl phenyl ether into the corresponding propenyl ethers in benzene solution in the presence of catalytic amounts of *trans*-PtH(ClO₄)(PPh₃)₂ (II). These reactions have been found to occur similarly in methylene chloride, chloroform, and acetone with II as catalyst as well as with *trans*-PtH(NO₃)(PPh₂Me)₂ (III), *trans*-[PtH(PPh₃)₂-(acetone)]⁺BF₄⁻, and *trans*-PtH(SnCl₃)(PPh₃)₂, but not with *trans*-PtHCl(PPh₃)₂, *trans*-[PtH(PPh₃)₂L]⁺BF₄⁻ (L = CO, PPh₃), nor *trans*-[PtMe(PMe₂Ph)₂(acetone)]⁺PF₆⁻ (see Table II and Experimental Section). Unidentified precipitates appeared gradually as the isomerization reaction proceeded in the reaction using II in benzene solution and *trans*-PtH-(SnCl₃)(PPh₃)₂ in CH₂Cl₂ and acetone solution. The reaction of allyl methyl ether with II as catalyst in benzene-methanol or CH₂Cl₂-methanol solvent gave no propenyl methyl ethers, but instead an amount of $\text{CH}_3\text{CH}_2\text{CH}(\text{OME})_2$ was produced, equivalent to the amount of II used. It is of interest to note in Table II that the isomerization reaction is highly specific during the early stages in that the resulting propenyl methyl or phenyl ethers have very high *cis*:*trans* ratios for all cases except for the reaction with *trans*-PtH-(SnCl₃)(PPh₃)₂. This may be compared to the *cis*-selective isomerization of allyl alkyl ethers with basic catalysts^{6,7} and also to the nonstereospecific isomerization of the same olefins with Fe(CO)₅ in the presence of light.^{7,8} The conversion of *cis*- to *trans*-propenyl methyl ether was found to

(6) T. J. Prosser, *J. Amer. Chem. Soc.*, **83**, 1701 (1961).

(7) A. J. Hubert, A. Georis, R. Warin, and P. Teyssie, *J. Chem. Soc., Perkin Trans.*, **1**, 366 (1972).

(8) P. W. Jolly, F. G. A. Stone, and K. MacKenzie, *J. Chem. Soc.*, 6416 (1965).

Scheme I

Table I. Results of the Reaction between PtD and (CH₂=CHCH₂)₂O in CH₂Cl₂ (0.4 ml)

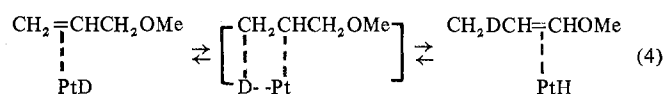
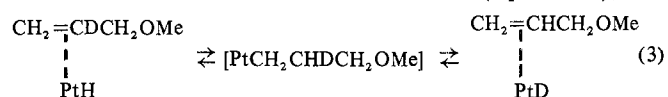
X	PtD _x H _{1-x} (X)(PR ₃) ₂			Amt of (C ₃ H ₅) ₂ O, mmol	[(C ₃ H ₅) ₂ O]/[PtD]	%	%	CH _{3-y} D _y CH _{2-z} D _z CHO ^b	
	PR ₃	x	mmol					C ₃ H ₅ DO ^a	C ₃ H ₄ D ₂ O ^a
ClO ₄	PPh ₃	0.75	0.183	0.183	1.0	70	1.5	0.46	0.22
			0.216	0.817	3.8	70	1.5	0.45	0.25
NO ₃	PPh ₂ Me	0.85	0.290	0.327	1.1	61	5	0.39	0.29
			0.290	1.730	6.0	51	8	0.40	0.20

^a Determined by mass spectra. ^b Determined by nmr spectra.

proceed more slowly in CH₂Cl₂, CHCl₃, or acetone in the presence of II or III.

The isomerization reaction was then performed using CH₂=CH_{0.15}D_{0.85}CH₂OMe and II in benzene-*d*₆ or CDCl₃. Deuterium distribution in the products was determined by nmr spectroscopy. In benzene, 0.55-atom deuterium incorporation at the terminal methyl group was calculated from the combined peak areas of the methyl resonances of *cis* (91%) and *trans* (6%) isomers relative to the peak areas of *O*-methyl signals. Similarly, 0.12 atom of deuterium incorporation was found at C₂ of the *cis*-propenyl methyl ether. Although the similar chemical shifts for the C₂ proton of allyl methyl ether and the =CHO- proton of the *cis* product precluded the accurate estimation of the deuterium content in the latter, the combined peak areas of these two resonances suggest that at least some 0.20 atom of deuterium is incorporated in the =CHO- group. The signals due to the C₂ and =CHO- protons of the *trans* isomer are too weak to determine accurately the deuterium content. When this same isomerization reaction was performed in CDCl₃, a similar deuterium distribution pattern was observed for the mixture of *cis* (73%) and *trans* (8%) products; 0.56 atom of deuterium is incorporated at the combined methyl groups, 0.17 atom of deuterium is incorporated at C₂, and at least some 0.14 atom of deuterium is incorporated in the =CHO- group of the *cis* isomer. An accurate estimation of the deuterium content in the C₂ and =CHO- groups of the *trans* isomer could again not be made.

The migration of an appreciable amount of deuterium from C₂ to the terminal carbon may be explained by assuming anti-Markownikov addition of the Pt-H bond across the C=C bond, which is then followed by elimination of Pt-D and attack of deuterium on the terminal carbon (eq 3 and 4),



although the intermediate involved in eq 4 may not be as simple as that described in eq 1 (see later). In eq 3, the equilibrium position may well be in favor of the system PtD + CH₂=CHCH₂OMe judging from the higher deuterium content in the methyl group than at C₂ of the propenyl methyl ethers. A similar 1,2 deuterium shift was reported⁹ to occur in the isomerization of vinyl- and allyl-deuterated 1-olefins with a Rh(III) catalyst. The occurrence of both Markownikov and anti-Markownikov additions of M-H across the terminal C=C bond was also suggested in the isomerization of butene-1 with some metallic complexes,^{4,10}

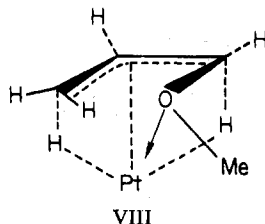
(9) J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **88**, 3491 (1966).(10) C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 2994 (1972).

Table II. Isomerization of Allyl Methyl Ether (0.22 mmol) into Propenyl Methyl Ethers

Catalyst	Amt, mmol	Solvent	Amt, ml	Time, min	Conversion, %		
					Cis	Trans	Cis:Trans
PtH(ClO ₄)(PPh ₃) ₂	0.0037	C ₆ H ₆	0.4	60	~100	Trace	
			0.0061	CH ₂ Cl ₂	0.4	6	38
	0.0061	Acetone- <i>d</i> ₆	0.4	7	49	7	8.5
				60	68	15	4.5
[PtH(PPh ₃) ₂ (acetone)] ⁺ BF ₄ ⁻	0.0060	Acetone- <i>d</i> ₆	0.3	5	48	2	14
				30	86	7	12
	0.0085	CH ₂ Cl ₂	0.4	35	14	7	0.5
				15	5	5	1
PtH(NO ₃)(PPh ₂ Me) ₂	0.0091	CH ₂ Cl ₂	0.4	90	43	Trace	
				1 day	86	2.5	35

including Pt(II) compounds, and in the reaction of propene-*d*₆ with HCo(CO)₄.¹¹

The reaction described by (4), with high *cis* selectivity during the early stages of the isomerization, could be a kinetically controlled reaction due to the specific interaction of oxygen with the platinum atom in the activated complex VIII. Thus, a σ -alkylplatinum(II) species such as PtCH-



(CH₃)CH₂OMe does not necessarily have to be formed during the reaction. The process corresponding to the reverse of eq 4, involving a platinum(II)-deuterido complex may be responsible, in part, for the incorporation of some deuterium at the =CHO- group. The total reaction mechanism, however, may be much more complicated, since the above does not adequately explain the ready isomerization of allyl methyl ether with *trans*-PtH(SnCl₃)(PPh₃)₂ which gives a different stereoisomer distribution pattern. Furthermore, the mechanism of the *cis* to *trans* conversion of propenyl methyl ethers with II or III still remains to be investigated.

The reaction of allyl methyl ether with II or III in the presence of methanol may involve nucleophilic attack by methanol on the coordinated C=C bond^{12,13} of propenyl methyl ethers bound to a cationic PtH⁺ moiety to form an intermediate, HPtCH(CH₃)CH(OMe)₂. This may then decompose, possibly by the action of H⁺, to give CH₃CH₂CH(OMe)₂.

Isomerization of Butene-1. Butene-1 was also converted readily to butene-2 at room temperature in the presence of catalytic amounts of II, III, or *trans*-[PtH(PPh₂Me)₂(acetone)]⁺BF₄⁻ (IX) in methylene chloride. No stereospecificity was observed in any case, the *trans*:*cis* ratio being approximately 3-2. Interestingly, the platinum(II)-containing complexes which were recovered after all the butene-1 had been consumed (1 mmol of butene-1 relative to 0.08 mmol of IX) were found to be a mixture of *trans*-[PtH(PPh₂Me)₂L]⁺ and *trans*-[Pt-*n*-Bu(PPh₂Me)₂L]⁺ (L may be the solvent, acetone, or olefins) as identified by forming the corresponding pyridine complexes.^{2,14} *trans*-[Pt-*n*-Bu(PPh₂Me)₂(py)]⁺BF₄⁻

(11) P. Taylor and M. Orchin, *J. Amer. Chem. Soc.*, **93**, 6504 (1971).

(12) Several π -olefinplatinum(II) complexes are known to be susceptible to nucleophilic attack by OR, OAc, etc. to give a σ -alkylplatinum(II) complex. See also ref 13.

(13) R. J. Cross, *Organometal. Chem. Rev.*, **2**, 97 (1967).

(14) H. C. Clark and H. Kurosawa, unpublished results.

has been prepared previously by the continuous bubbling of butene-1 through a methylene chloride solution of IX, followed by the addition of pyridine.² This result clearly indicates that the addition of the Pt-H bond across C=C of the butene-1 also occurs in both Markownikov and anti-Markownikov directions. The above facile isomerization of butene-1 may be compared to the fact that *trans*-PtDCl-(PEt₃)₂ reacted with octene-1 at 130° by an anti-Markownikov addition without any indication of the formation of isomerized octenes¹⁵ and also to the fact that hexene-1 was isomerized by *trans*-PtHCl(PEt₃)₂ at 172° in a sealed tube with rather low yields of isomerization products.⁴

Experimental Section

Starting materials were obtained as follows.

Olefins. Allyl phenyl ether was obtained from Eastman Kodak Co., and butene-1 from Matheson of Canada Ltd. Allyl methyl ether and diallyl ether were prepared by standard methods.

2-Deuterated allyl methyl ether was prepared as follows. A Diels-Alder adduct of methyl acrylate and anthracene was treated with a twofold excess of NaH in THF under nitrogen at room temperature for 4 hr; then a fourfold excess of methanol-*O-d* was added to the solution. The solvents were removed under reduced pressure, and the resulting solids were extracted with ether. The white crystals obtained on evaporation of the ether were reduced by LiAlH₄ in a manner similar to that reported¹⁶ as giving the Diels-Alder adduct of CH₂=CDCH₂OH and anthracene. This adduct was further treated with NaH followed by the addition of methyl iodide to give an *O*-methylated product, which was finally allowed to pyrolyze at 350° to give CH₂=CDCH₂OMe (bp 43°) (16% yield on the basis of the starting material). The proton nmr spectrum in CDCl₃ showed that C₂ contains 15 ± 5% protium and 85 ± 5% deuterium (τ 4.2, multiplet). Other resonances appeared at τ 4.8 (m, 2) (terminal olefinic protons), 6.1 (m, 2) (allylic protons), and 6.67 (s, 3) (*O*-methyl protons).

Platinum(II) Hydrides and Deuterides. The preparations of *trans*-PtH(ClO₄)(PPh₃)₂¹⁷ (II), *trans*-PtH(NO₃)(PPh₂Me)₂¹⁸ (III), *trans*-[PtH(PPh₂Me)₂(acetone)]⁺BF₄⁻ (IX), *trans*-PtH(SnCl₃)(PPh₃)₂¹⁹, *trans*-[PtH(PPh₂)₂L]⁺BF₄⁻ (L = acetone, CO, and PPh₃)²⁰ and *trans*-[PtMe(PMe, Ph)₂(acetone)]⁺PF₆⁻²¹ have been reported previously. *trans*-PtDCl(PPh₃)₂ was prepared by allowing Pt(PPh₃)₄ in benzene to react with DCl which was generated from CH₃COCl and methanol-*O-d*. The deuterium content of *trans*-PtD(ClO₄)(PPh₃)₂ (II) was estimated using infrared spectroscopy as follows. IIid was converted to *trans*-[PtD(PPh₃)₂(CO)]⁺ClO₄⁻¹⁷ whose infrared spectrum was examined in CH₂Cl₂ using a NaCl solution cell (0.1 mm). The peak size of ν (C=O) at 2087 cm⁻¹, due to *trans*-[PtH(PPh₃)₂(CO)]⁺ClO₄⁻

(15) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968).

(16) P. D. Bartlett and F. A. Tate, *J. Amer. Chem. Soc.*, **75**, 92 (1953).

(17) I. V. Gavrilova, M. I. Gel'fman, N. V. Ivannikova, and V. V. Razumovskii, *Russ. J. Inorg. Chem.*, **16**, 596 (1971).

(18) H. C. Clark and H. Kurosawa, *J. Organometal. Chem.*, **36**, 399 (1972).

(19) J. C. Bailar, Jr., and H. Itatani, *J. Amer. Chem. Soc.*, **89**, 1592 (1967).

(20) J. J. Howard, M.Sc. Thesis, University of Western Ontario, 1971.

(21) M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, **11**, 1269 (1972).